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LATTICE PARAMETER CHANGES DURING THE
ANNEALING OF QUENCHED ALUMINUM

by
Casimir Eubig

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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Casimir Eubig

entitled Lattice Parameter Changes during the Annealing of Quenched Aluminum

be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

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ABSTRACT

A study of the defects quenched in aluminum was performed by measuring simultaneous changes in the x-ray lattice parameter and in the line shape of the (333) Bragg reflection. Experimental techniques were developed to measure lattice parameter changes to one part in $10^6$ and to permit annealing the sample at high temperatures in between successive measurements. Isochronal anneals were carried out, and most of the annealing is found to take place in two stages which occur at the same temperatures as those observed previously by means of resistivity measurements. Lattice parameter changes are explained by considering the relaxation of the crystal about the different defects. Bragg line intensity and half-width changes are found consistent with theories on the effect of crystal defects on x-ray diffraction. Large vacancy clusters, especially dislocation loops, are found to have a large effect on the parameters studied. The observed behavior of large vacancy clusters in the present study was consistent with electron microscopy data.
CHAPTER 1

INTRODUCTION

The quenching technique has been employed extensively as a means of obtaining a supersaturation of defects in metals to investigate the physical properties and kinetics of these defects. The primary defects were confirmed as vacancies in a large number of cases in metals. It is possible, by thermal annealing, to induce the migration of supersaturated vacancies to sinks, and thus effect the recovery of the metal to its original state. It was also found, however, that for many vacancies this process was not direct, but that it involved the formation of a number of intermediate defect aggregates. Thus the formation and behavior of divacancies and higher vacancy clusters, voids, dislocation loops, and stacking faults have been the objects of numerous investigations.

One of the metals whose quenched-in defect properties have been extensively studied is aluminum. Simmons and Balluffi\textsuperscript{1} have shown that the predominant defects at thermal equilibrium in aluminum are vacancies, and have measured their concentration as a function of temperature. Extensive resistometric research on quenched aluminum and aluminum alloys has been performed as reviewed by Federighi.\textsuperscript{2}
Furthermore, perfect (prismatic) and faulted (Frank sessile) dislocation loops and voids\textsuperscript{3,4,5} were observed directly in aluminum by electron microscopy.

In general, electrical resistivity measurements turn out to be an excellent way to follow the behavior of defects undergoing thermal anneal. These measurements give changes in the concentration of a defect with a high degree of accuracy with relative ease. However, electrical resistivity measurements have the disadvantage that all defects increase the resistivity. As a result, it often becomes difficult or impossible to separate the effects of different defects. This is one reason why, even though the general features of annealing of defects in aluminum are well known, there are still a number of details which have not been conclusively established. Some of these difficulties would be resolved by taking measurements, with experimental techniques, that are sensitive to the differences among the various possible processes.

Microscopy techniques are the most effective way of identifying defects. However, because of the restrictions peculiar to electron microscopy, such as preparation of suitable samples prior to examination, the method cannot be adapted readily to follow the annealing behavior of defects in most cases. The x-ray diffraction technique, on the other hand, is a method which can be made sensitive to the type and amount of distortion of the lattice caused by the
presence of defects. The technique involves measurements of changes in lattice parameter and in half-width and intensity of x-ray Bragg reflection lines at various stages of anneal. Even though the information content of such measurements is potentially much greater than in resistivity measurements, this technique has not yet been applied to the study of annealing of quenched-in defects in metals. It has been applied successfully to the study of metals following radiation damage\textsuperscript{6,7,8} and cold work.\textsuperscript{9,10}

A look at the measurements of lattice parameter changes by Sepp et al.\textsuperscript{7} shows $\Delta a/a$ typically accurate to $\pm 4 \times 10^{-5}$. Using data of Simmons and Balluffi\textsuperscript{1} on the equilibrium concentration of vacancies in aluminum, and assuming that about half of the vacancies are lost after a water quench from 600°C, we can estimate a concentration of about $2 \times 10^{-4}$ vacancies remaining. This results in a maximum possible change in $\Delta a/a$ of $7 \times 10^{-5}$. In order to apply the x-ray diffraction technique to the study of metals with quenched-in vacancies, it is thus necessary to measure $\Delta a/a$ with an accuracy of at least $\pm 1 \times 10^{-6}$. It is the purpose of this work to develop techniques to achieve the necessary accuracy, and to apply these techniques to study the mechanism of annealing of quenched-in vacancies in aluminum.
2.1 Sample Preparation

The aluminum samples used are oriented single crystal foils. They are 0.040 inch wide, 0.100 inch long, and 0.010 inch thick. These have to be suitably shaped for mounting in a specially designed x-ray cryostat. They must also be sufficiently small so that quenching strains\(^{11}\) are minimal while fast quenching rates are maintained. A high purity aluminum (99.999%) single crystal, $\frac{1}{2}$ inch in diameter, is grown by the Bridgman method in a spectroscopic purity graphite crucible in a vacuum. The crystal is then cut parallel to its \{111\} planes into 0.025 inch thick slices with a spark cutter. The slices are then shaped as shown in Fig. 1 with a special spark cutting tool (Fig. 2). Electrical leads are then attached to the edge of each slice with silver epoxy, and the junction is covered with liquid porcelain (Fig. 1). The slice is then electropolished\(^{12}\) to remove the damage to the surface and release the samples from the slice. Thus the final sample shape and dimensions are obtained. Each sample then undergoes a chemical cleaning.\(^{13}\) A 0.005 inch diameter chromel-alumel thermocouple is
Figure 1. Samples as Shaped by Spark Cutter just Prior to and After Electropolishing

(a) Single Crystal Slice          (b) Finished Samples
Figure 2. Spark Cutter Tool for Cutting Sample Shapes Out of Single Crystal Slice
then spot-welded to one of its halves. This half becomes the "dummy sample" and is used to monitor the temperature of the sample during annealing and quenching. Also, when the sample is inserted inside the cryostat it is clamped at this end.

2.2 Quenching and Mounting of the Sample

A sample is annealed and quenched inside a modified Greninger\textsuperscript{14} gas quenching furnace. The sample is suspended inside a tantalum heating coil and then annealed in vacuum (10^{-6} \text{ mmHg}) at the quenching temperature of 600°C for one or two hours. It is then quenched by the introduction of helium gas into the furnace. The gas is precooled to liquid nitrogen temperature and is under a line pressure of 30 pounds per square inch. The sample is immediately transferred to a liquid nitrogen bath. Quenching rates of up to 5000°C/sec are obtained. The temperature during the quench is recorded by an oscilloscope camera, and it is found that the quenching rate is constant during the first 200°C drop. From the work of Speich and Fisher\textsuperscript{15} on rapid heating and quenching techniques, it was determined that, under the quenching conditions described above, the temperature should remain uniform throughout the sample during the entire quench.

The cryostat design permits placing the sample inside it after quenching without allowing the sample to
warm up. This was accomplished by securing the sample in a combination clamp and transfer mount (5 - Fig. 3) while under liquid nitrogen. The clamp consists of two parts (4 and 19) which slide along the top of the transfer mount. A channel (20) is machined into part 4 to guide precise positioning of the samples. Part 4 is aligned so that the axis of rotation of the cryostat lies along the inside surface of the channel. The surface of the sample facing the x-ray beam rests against this surface. Also, the x-ray beam is adjusted to go through the axis of rotation of the cryostat. These alignments insure that the x-ray beam always strikes the same portion of the sample as the sample is rotated. With adjustments completed, part 4 is secured in place with screws (3).

The sample is first slid into the channel in part 4 and positioned in the window (21) in the transfer block. Then the upper half of the sample (the "dummy sample") is clamped between parts 4 and 19 and secured by screws (18). The whole assembly can now be lifted out of the liquid nitrogen and fastened to the top of the vertical-tilt goniometer (10) inside the cryostat which has been precooled to liquid nitrogen temperature.

2.3 Lattice Parameter Measurements

The technique used was essentially that developed by Bond\textsuperscript{16} to measure the lattice parameter of nearly perfect
Figure 3. Liquid Nitrogen Cryostat and Sample Mount

(a) End-on View of Sample Mount
crystals to a few parts in a million. In this case the task is somewhat simplified in that all that is necessary is to measure changes in the lattice parameter with the same precision. On the other hand, a problem arises over obtaining crystals perfect enough to perform single crystal x-ray measurements. Special problems are also encountered by the necessity of getting the sample ready for measurement after first quenching it, as well as by the necessity of annealing the sample in between the taking of successive measurements.

The differentiated form of the Bragg equation

\[ \Delta \theta = -(\Delta a/a) \tan \theta \]

shows that high Bragg angles are most sensitive to changes in the lattice parameter. With aluminum at -195°C and CuK\textsubscript{a1} radiation, a Bragg reflection at \( \theta = 83^\circ 0' \) from the \{333\} planes can be used. To measure \( \Delta a/a \) to \( \pm 10^{-6} \) one then has to measure changes in the Bragg angle to about \( \pm 2 \) seconds of arc.

Angle measurements have to be taken over only a small range. Stage micrometers (E - Fig. 4) (2 mm divided into 200 parts) are used for this purpose, mounted at the end of an 18.5 centimeter long arm (F - Fig. 4). The stage micrometer has to be read to at least 0.0015 mm. A microscope with an eyepiece reticle having 0.1 mm divisions is used as a vernier to read the micrometer to 0.0005 mm. The measuring arm (F - Fig. 4) is fastened to the bottom of the
Figure 4. A Top View of the Measuring Apparatus
metal sleeve (14 - Fig. 3). This metal sleeve also fits inside a pair of bearings, the top of which is shown (15 - Fig. 3). These support the cryostat and allow it and the attached measuring arm to rotate freely. The measuring arm and cryostat are driven by micrometer heads (G - Fig. 4).

To measure the position of the Bragg angle, x-rays reflected from the crystal are counted by a G.M. tube (C - Fig. 4) for different angular positions of the cryostat as it is rotated through the Bragg angle. The output of the x-ray tube is monitored by a second G.M. tube (B - Fig. 4) which measures CuKα radiation reflected from an aluminum crystal set in a fixed position.

It was found that the x-ray line width at one-half maximum varied from about 500 to 900 seconds of arc. This means that the change in the line position has to be measured consistently to one part in 300 to 500 of its half-width. Ogilvie had found that it is possible to determine the peak position of a broad diffraction line by fitting a parabola to five points near the top of the intensity curve by the method of least squares. This technique was adapted to give satisfactory determinations of peak position changes in this experiment. A simple computer program is employed for the parabolic curve fit of 15 to 20 points of intensity measurement. The intensity measurements taken are accurate to within one percent and are all within 25% of the peak value.
2.4 Obtaining Suitable X-Ray Rocking Curves

Noggle and Koehler\textsuperscript{18} examined single crystal specimens of 99.99\% aluminum grown from a melt and those grown by the strain anneal method. In both types of crystal grown they found the presence of some small angle grain boundaries. In the present case, the task of obtaining crystals relatively free of small angle boundaries is even more difficult because the higher purity of the crystal enhances the tendency for polygonization.\textsuperscript{19}

In order to overcome this difficulty, an adjustable slit system is devised to place the x-ray beam in a region of the sample free from small angle grain boundaries. In the assembly shown in Fig. 5, each of the slit sides can be adjusted independently to within 0.0005 inch. By crossing two such assemblies, a slit with adjustable height, width, and position can be obtained. Two such slits (A - Fig. 4) mounted 20 inches apart make up the collimating system for the x-ray beam. The amount of adjustment possible with the slit system is limited by the focal spot size of the x-ray tube. A Norelco fine focus x-ray diffraction tube with a projected focal spot size of 0.016 inch by 0.032 inch (6 degree take-off angle) was used in this experiment. After the sample is quenched, secured in the cryostat, and the vertical tilt of the sample (discussed in section 2.6) is adjusted, the sample chamber (16 - Fig. 3) of the cryostat is sealed off (1 - Fig. 3), and the adjustment of the slit
Figure 5. Adjustable Slit Assembly
system can proceed. A series of Bragg reflected spots taken on film (D - Fig. 4) with varying position and size of the x-ray beam is shown in Fig. 6. The last spot in the series shows an absence of any larger subgrain boundaries, and the resulting rocking curve is sufficiently smooth and symmetrical to allow a measurement of the Bragg angle changes with the desired precision.

2.5 Liquid Nitrogen Cryostat—Temperature Control and Measurement

It is necessary for the cryostat to hold the sample at liquid nitrogen temperature during the x-ray exposures and to provide for the heating of the sample to temperatures as high as 250°C in between measurements. A change in the temperature of aluminum by 0.1°C results in a lattice parameter change of approximately one part in 10⁶. It was found possible only occasionally, however, to keep the temperature fluctuation of the sample within acceptable limits during the measurement of one Bragg angle. Since it takes a number of days to collect the data needed for an average run it is necessary to monitor the temperature of the sample throughout the run.

The cryostat consists of two vacuum-tight chambers. The coolant chamber (29 - Fig. 3) is formed by two concentric copper cylinders sealed off at both ends except at the liquid nitrogen inlet (12) and overflow (17). The coolant chamber is attached to a copper pedestal (31). The space
### Figure 6. Effect of Slit Adjustment on the Reflected X-Ray Beam

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<th>SLIT WIDTH (INCH)</th>
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<tr>
<td>(FRONT)</td>
<td>(REAR)</td>
<td>.020</td>
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<td>.020 x .010</td>
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inside the sample chamber (16) contains the tilt goniometer which is silver soldered to the top of a \( \frac{1}{4} \) inch diameter 0.010 inch thick wall stainless steel tube (28) which in turn is attached to the pedestal (31).

Three copper-constantan thermocouples are attached to the tilt goniometer in the positions shown (9 - Fig. 3). As long as the temperature changes by the same amount at all three thermocouples, it is reasonable to assume it changes by this same amount at the sample. In order to insure temperature uniformity the sample chamber (16) is filled with helium gas. In a vacuum the temperature of the sample is sensitive to the thermal contact resistance between sample and clamp. However, gold plating the sample clamp (5) and goniometer parts (24, 25) and introducing helium gas into the sample chamber reduces the thermal contact resistance to the point where no effect on it due to the annealing treatments can be detected.

The bottom of the vertical tilt goniometer has an insulated heater wire (11 - Fig. 3) wound around it. This allows the sample to be annealed at temperatures up to 250°C, provided the sample chamber is first evacuated through tube 32. A thermocouple temperature controller keeps the temperature constant to a few degrees Celsius during anneal. The heating rate at 12 watts is 17°C/min. To cool the sample, the heating current is interrupted and helium gas
is introduced into the chamber. A cooling rate of 31°C/min is obtained.

The cryostat assembly (31, 33, 14 - Fig. 3) rotates at the bearings (15). Thin-walled nickel bellows (35) allow for the contraction in length of tubing (12, 32, 17) due to cooling. The heater and thermocouple wires enter the sample chamber through an epoxy seal at the bottom of the pedestal (31). X-rays enter and leave the sample chamber through 0.0005 inch thick mylar windows (7). Vacuum is maintained by the use of a Wilson seal (34) and pressed indium O-ring seals (2, 8, 13, 30).

2.6 Sample Shift Corrections

After a cooling and annealing cycle the sample is not found at its exact previous position. This results in an apparent change in the Bragg angle. The sample clamping arrangement described above minimizes this shift. It is best to mount the sample on the end of a relatively large diameter tube (28 - Fig. 3), which together with tube (33) and sleeve (14) make up the main shaft of the cryostat. The coolant chamber (29) is attached to the outside rim of the pedestal (31) away from the central shaft. The main advantage of the present design of the cryostat is that annealing is performed without interrupting the liquid nitrogen flow, and only the smallest possible portion of the apparatus is affected by the heating.
The sample shift is thus minimized but not completely eliminated. Bragg angle changes must be separated from angular changes attributable to the sample shift. There are two sample motions that can be mistaken as a Bragg angle change: 1) the rotation of the sample around the axis of rotation of the cryostat, and 2) the rotation of the sample around an axis perpendicular to both the x-ray beam and the axis of rotation of the cryostat (the sample tilt).

It can be seen from Fig. 4 that a Bragg reflection can be obtained from the same crystal planes at an angle of \( \pi - 2\theta \) on either side of the incident x-ray beam. (\( \theta \) is the Bragg angle.) When the Bragg angle changes, the angle between the incident x-ray beam and the Bragg reflections on the left and right sides of the x-ray beam will both either decrease or increase. However, if the sample were to undergo a rotation around the axis of the cryostat, the angle between the x-ray beam and the Bragg reflection to the right would apparently change in one direction (increase or decrease), while the corresponding angle to the left would undergo an apparent change in the opposite direction. It is thus possible to eliminate the changes arising from sample rotations around the axis of the cryostat by detecting the Bragg reflection on both sides of the x-ray beam. Sample rotations as high as 40 seconds of arc occurred during the runs, though most of the rotations were below 10 seconds of arc.
The method mentioned above cannot distinguish between real Bragg angle changes and apparent Bragg angle changes due to variations in the tilt of the sample. One can follow Bond’s analysis of the relation among the tilt angle $\Delta$, the measured Bragg angle $\theta'$, and the true Bragg angle $\theta$. Starting with the relation

$$\sin \theta = \cos \Delta \sin \theta'$$  \hspace{1cm} (1)

and assuming $\theta$ does not change while the tilt angle $\Delta$ does, one obtains

$$\delta\theta' = \tan \Delta \tan \theta' \delta \Delta.$$  \hspace{1cm} (2)

For small $\Delta$, $\tan \theta' \approx \tan \theta$. Then $\tan \Delta$ can also be replaced by $\Delta$ and the sample tilt correction becomes

$$\delta\theta' = \tan \theta \Delta \delta \Delta.$$  \hspace{1cm} (3)

$\Delta$ involves the sum of two errors: one arising from the fact that the reflecting planes of the crystal are not parallel to the rotation axis of the cryostat, and another arising from the fact that the collimated x-ray beam is not perpendicular to this axis. Bond shows that for an accuracy in the lattice parameter of one part in a million $\Delta$ must not exceed $\pm 4.8$ minutes of arc. A fine adjustment of the take-off angle of the x-ray beam is made bringing the misalignment of the collimated x-ray beam to within 0.6 minutes of arc. Then $\Delta$ and $\delta \Delta$ only arise from the misalignment of the
sample's crystal planes. $\Delta$ and $\delta\Delta$ are measured photographically. By moving a sheet film (D - Fig. 4) in front of the collimator opening, one obtains a line establishing the position of the incident x-ray beam. Then placing the film in front of the appropriate G.M. tube while the crystal is situated at the Bragg angle, one obtains a spot establishing the position of the reflected x-ray beam. Recording the vertical position of the Bragg reflection on film each time the Bragg angle is measured, one can obtain $\Delta$ and $\delta\Delta$ values by making measurements on the film under a microscope.

It can be seen from Eq. (1) that the total crystal tilt has to be kept small to minimize the corrections. To insure this, the vertical tilt goniometer (10 - Fig. 3) is built into the cryostat. This allows the crystal planes of the sample to be adjusted parallel to the axis of rotation of the crystal. Adjustment is monitored by using a sheet film (D - Fig. 4). The vertical tilt goniometer consists of a movable part (24 - Fig. 3) to which the sample clamp and transfer mount (5 - Fig. 3) is attached. The matching surfaces of parts 24 and 25 (Fig. 3) have a curvature that allows the sample to be rotated around an axis in the front surface of the sample where the x-ray beam strikes. The goniometer is driven through the opening in the top of the cryostat by turning the shaft (22 - Fig. 3) which turns the worm gear (27) and drives the "one tooth" gear (26) attached
to the bottom of part 2\textsuperscript{4}. This arrangement permits the tilt of the sample to be adjusted to within about 0.1 minutes of arc. The goniometer is locked in position with set-screws (23 - Fig. 3) after adjustment. Tilt correction to the Bragg angle changes are thus reduced to less than a few seconds of arc in almost all cases.
A check was performed on the reliability and consistency of the method used to determine the center of the x-ray line. An annealed sample was placed in the cryostat. The Bragg reflection was scanned three times. A different number of data points over the same interval were taken each time (top of Fig. 7), and the results shown demonstrate the reliability of the method. The error bars represent the probable error of the average of data deviations from the parabolic fit.

Two null runs were made on annealed but unquenched samples. A third run was performed on a sample quenched from 300°C. The data obtained are shown in the lower half of Fig. 7. These results show that there is no net change in the lattice parameter to within two parts in \(10^6\) during anneal of a specimen without measurable excess vacancies. Consistency of line width and peak intensity measurements, deduced from the fitted parabola, can also be seen.

Three runs on samples quenched from 600°C are shown in Figs. 8, 9 and 10. The sample in run 3 was inserted into the liquid nitrogen bath in a horizontal position so that
Figure 7. Null Runs

Top of figure: Fitting parabola to experimental data after scanning Bragg peak three times. B1 and B2 are made up of alternate data points from Scan B. In a similar way C1, C2, and C3 are formed from Scan C. (B + C) combines data from Scan B and Scan C.

Bottom of figure: Data taken with right G.M. tube —Δ—, left G.M. tube —○—.
Run 3: Quench temperature 300°C; quench rate 3000°C/sec; specimen thickness 0.008 inch.
Figure 7. Null Runs

**Annual Temp.**
- 200°C
- 100°C
- 0°C

**Δa/α (x 10^-6)**
- 10
- 0
- -10

**Bragg Line Half-Width (min of arc)**
- 40
- 30
- 20

**Bragg Line Peak Int. (% change)**
- 6
- 3
- 0

**Run 1**
- Scan A
- Scan B
- Scan C

**Run 2**
- Scan A
- Scan B
- Scan C

**Run 3**
- Scan A
- Scan B
- Scan C

**Number of data points:**
- 55
- 11
- 11
- 33
- 11
- 11
- 22
- 12

**Δa/α (x 10^-6)**
- 10
- 0
- -10
Figure 8. Run 4 Isochronal Annealing After Quenching, 15 Minutes at Each Temperature

--- right G.M. tube; --- left G.M. tube.
Quench temperature 600°C; quench rate 4400°C/sec; specimen thickness 0.012 inch.
Figure 8. Run 4 Isochronal Annealing After Quenching, 15 Minutes at Each Temperature
Figure 9. Run 5 Isochronal Annealing After Quenching, 15 Minutes at Each Temperature

—Δ— right G.M. tube; —○— left G.M. tube. Quench temperature 600°C; quench rate 5400°C/sec; specimen thickness 0.012 inch.
Figure 9. Run 5 Isochronal Annealing After Quenching, 15 Minutes at Each Temperature
Figure 10. Run 6 Isochronal Annealing After Quenching, 15 Minutes at Each Temperature

— right G.M. tube; — left G.M. tube.
Quench temperature $600^\circ C$; quench rate $3000^\circ C/\text{sec}$; specimen thickness 0.009 inch.

— obtained by taking additional data in the wings of the Bragg reflections and fitting them with a Cauchy function.
Figure 10. Run 6 Isochronal Annealing After Quenching, 15 Minutes at Each Temperature
the specimen was cooled from one side to check on how thermal strains after quenching affect the measurements.

Additional data were taken during run 6 (Fig. 10) consisting of intensity measurements extending partly into the tail portion of one side of the x-ray peak. Assuming the peak to be symmetrical, a very good fit to the data is obtained with a Cauchy function

\[ y = a - \frac{b}{(c - (x - d)^2)} \]

Changes in the shape of the x-ray Bragg peak during annealing are shown in Figs. 11 and 12. Following the designation used by Federighi, \(^2\) Q-1 refers to the low temperature stage of annealing after quenching while Q-2 refers to the higher temperature stage. Since measuring widths at half intensity involves an extrapolation of the parabola, half-widths obtained directly from the fitted Cauchy curves are also shown in Fig. 10. Furthermore, the area under the fitted Cauchy curves is shown as the integrated peak intensity in Fig. 10.

The results obtained from fitting Cauchy curves were also used to check on the reliability of the parabola method for determining the position of the x-ray line. The average of standard deviations for parameter \(d\), the center of the Cauchy curves, was found to be \(0.9 \times 10^{-6}\) (in terms of \(\Delta a/a\)) with values ranging from \(0.7\) to \(1.1 \times 10^{-6}\). The standard deviations for the value of the center of the parabola were
Figure 11. Changes in the Shape of the X-Ray Bragg Peak During Run 6, State Q-1 Annealing
Figure 12. Changes in the Shape of the X-Ray Bragg Peak During Run 6, Stage Q-2 Annealing
an order of magnitude larger, yet values of the center of the x-ray peak found both ways all agreed to within ±1.5 \times 10^{-6}. A further check was performed by separating the data used to obtain the position of each x-ray peak in run 6 into two groups made up of alternate data points. This gave two independent determinations of the peak center for each x-ray peak. The distribution of differences between each pair of peak centers was found to be Gaussian. The maximum difference found was 3 \times 10^{-6} (in terms of \Delta a/a) with 50\% of the differences being less than 1 \times 10^{-6}. 
CHAPTER 4

DISCUSSION

Most of the annealing during runs 4, 5, and 6 takes place in two stages which occur at the same temperatures as those observed by Panseri and Federighi. However, variations in annealing behavior of the measured parameters exist, and those should be explained in terms of the different types of defects, their sizes, and concentrations present after quenching.

4.1 Lattice Parameter Changes

Stage Q-2 annealing in aluminum has been studied extensively by electron microscopy techniques, and most of the defects annealing out during this stage are known. The major types of these defects are prismatic \((a/2 \langle 110 \rangle)\) or perfect dislocation loops, stacking fault \((a/3 \langle 111 \rangle)\) loops, and octahedral voids with \{111\} surfaces. Small clusters of less than about \(10^3\) vacancies may also be annealing, although these do not show up under the electron microscope. Shimomura and Edington and Smallman found that these three types of defects anneal at different temperatures and in relatively sharp stages (Fig. 13). Since
Figure 13. Recovery of Quenched Aluminum During Stage Q-2 Annealing
the annealing stages for the different defects overlap, a mixture of defects describes adequately the broad annealing range seen in the lattice parameter changes during stage Q-2, run 6 (Fig. 13). On the other hand, the sharpness of stage Q-2 in run 5 (Fig. 13) indicates that only one predominant type of defect is annealing. An examination of the positions of stage Q-2 in runs 5 and 6 (Fig. 13) makes it apparent that the defect, annealing in run 5, is either the void or the perfect dislocation loop, as both were found by Shimomura\textsuperscript{23} and Edington and Smallman\textsuperscript{24} to anneal at a higher temperature than the faulted dislocation loop. In order to decide between these two possible defects in run 5, it is necessary to examine the lattice relaxations around the different types of defects.

Eshelby\textsuperscript{25} treats a cubic crystal with a uniform distribution of centers of dilatation producing elastic displacements of the form

\[ u(r) = \frac{C}{r^2} \]

where \( C \) represents the strength of the defect. He shows that the crystal volume change deduced from the change in the x-ray lattice parameter is equal to a uniform geometrical volume change deduced from a consideration of the relaxation of the crystal about all the defects. These results apply to vacancies.\textsuperscript{1} Analysis of the change in the lattice parameter observed in the present work indicates
that Eshelby's results can also be applied to vacancy clusters. One can see that a void can be considered as a center of dilatation that can be reduced to a point source with a displacement field varying as \(1/r^2\). Kroupa\(^{26}\) shows that displacement due to an infinitesimal dislocation loop also decreases with distance as \(1/r^2\). For a finite loop this behavior does not hold in the neighborhood of the dislocation line. However, at larger distances the displacement again decreases as \(1/r^2\). As pointed out by Krivoglaz and Hao,\(^{27}\) it is this asymptotic displacement field which largely controls the scattering intensity distribution pattern of the x-rays.

The amount of crystal relaxation around a vacancy, \(\Delta V_r\), is given by \(\Omega - \Delta V_{fV}\) where \(\Delta V_{fV}\) is the volume of formation of a vacancy and \(\Omega\) is one atomic volume. \(\Delta V_{fV}\) was measured for aluminum by Emrick and McArdle\(^ {28}\) as \(0.64\Omega\). Dislocation loops are collapsed vacancy disks,\(^ {26}\) so that the amount of crystal relaxation about a dislocation loop of radius \(r\) and Burgers vector \(b\) can be written as

\[
\Delta V_r(DL) = - \pi r^2 b + 2\pi r \Delta_{DL} / \Omega^{1/3}
\]

where \(\Delta_{DL}\) is the correction volume per atomic length of dislocation line to compensate for the incomplete collapse near the circumference of the loop. For a large loop of \(N\) vacancies with \(\Delta_{DL} \ll \Omega\), the second term becomes negligible and
\[ \Delta V_r (DL) = -N\Omega. \]

Considering \(2 \times 10^4\) vacancies and adding up the relaxation around them prior to their clustering, one obtains

\[ \sum \Delta V_r = -7 \times 10^3\Omega. \]

For the same vacancies forming a dislocation loop about 400Å in diameter, one finds that

\[ \Delta V_r (DL) = -20 \times 10^3\Omega. \]

Thus, a significant increase in relaxation is expected when vacancies cluster to form a dislocation loop. This can explain the decrease in lattice parameter observed in stage Q-1. During stage Q-2, as a dislocation loop shrinks, atoms are effectively removed from the surface and placed at the dislocation loop core. Thus, the net volume change of the crystal may be negligible. However, x-rays only see the effects of lattice relaxation about the defects, i.e., an increase in the volume equal to \(N\Omega\). This would again explain the large increase in the lattice parameter observed in stage Q-2.

To follow the expected behavior in the lattice parameter as vacancies form voids, one can express the amount of relaxation of the crystal about a large void of \(N\) vacancies with radius \(r\) as
\[ \Delta V_r(\text{void}) = -4\pi r^2 \Delta V_{\text{void}}/\Omega^{2/3} \]
\[ = -5N^{2/3} \Delta V_{\text{void}}, \]

where \( \Delta V_{\text{void}} \) is the volume change per atom at the surface as the surface of the void relaxes inward. Kiritani, Shimomura, and Yoshida,\(^5\) using a slow quench, observed voids with an average diameter of about 80Å. Such a void contains approximately \( 2 \times 10^4 \) vacancies. When one uses \( 0.36\Omega^{28} \) as the amount of crystal relaxation due to a vacancy one finds that a void consisting of \( 2 \times 10^4 \) vacancies would have a diameter of 68Å if one requires that the proportionate amount of total relaxation is maintained. This corresponds to an inward relaxation of the surfaces of the octahedral void by more than two interplanar distances. However, Shimomura\(^{23}\) observed that under the electron microscope the strain around voids is much smaller than that around dislocation loops. Furthermore, when one calculates the relaxation of atoms around the various forms of a tetravacancy\(^{29}\) which are thought to be the nuclei for the growth of faulted dislocation loops and voids,\(^{30}\) one is led to the conclusion that the collapse of the lattice around a void should be smaller than that found around a dislocation loop. If one assumes that the surfaces of the void are allowed to relax inward on the average one half of the spacing between \{111\} planes, \( \Delta V_{\text{void}} \equiv 0.5\Omega \) and for a void composed of \( 2 \times 10^4 \) vacancies one obtains
\[ \Delta V_r(\text{void}) = -2 \times 10^{-3} \Omega. \]

Comparing this to the relaxation around \(2 \times 10^4\) vacancies and the crystal relaxation when these form a dislocation loop, one can finally conclude that the large increase in the lattice parameter during stage Q-2 annealing of run 5 must be almost exclusively attributable to the disappearance of perfect dislocation loops. In stage Q-2, run 6, an appreciable increase in the lattice parameter is observed at a temperature lower than that in run 5. The size and direction of the change in the lattice parameter as well as the temperature at which it takes place (as previously discussed) are consistent with the presence of a significant number of faulted dislocation loops during run 6. The above observation also leads one to conclude that the decrease in the lattice parameter observed during stage Q-1 annealing in all runs is attributable to the formation or growth of dislocation loops. Voids are expected to produce an opposite effect on \(\Delta a/a\).

Electron microscopy observations have revealed that not only concentrations and sizes, but also types of vacancy clusters found after quenching depend very strongly on quenching conditions.\(^4,30,31\) The defects which are found to give rise to the annealing of the lattice parameter in the foregoing discussion must be consistent with the defects expected under the quenching conditions at the time of the different runs. Quench rate and atmosphere as well as
sample thickness are found to have particular significance in this investigation.

The quench rates used during this experiment, 3-5 × 10^3°C/sec, are relatively slow. Lowering the quench rate is known to result in a sharp decrease of dislocation loop density, while void density increases by a small amount. However, the determining factor for the formation of voids in aluminum is the atmosphere in which the sample is annealed prior to quenching. It is found that the presence of hydrogen in the aluminum sample has a significant effect on the early stages of nucleation of voids. Data on the solubility of hydrogen in aluminum are used to estimate the concentration of hydrogen under the present experimental conditions as 8 × 10^-9. When one considers the loss of hydrogen to sinks, 10^{13} cm^-3 of void density can be nucleated. Even though this is ten times higher than that found experimentally by Shimomura and Yoshida, this figure is a reasonable one when one considers the difference in outgassing conditions and other pertinent factors. On the other hand, Shimomura and Yoshida found a dislocation loop density of about 10^{14} cm^-3 which did not depend appreciably on annealing atmosphere, and was ten times the void density estimated.

In short, voids have a relatively small effect on the lattice parameter, and there are fewer of them present compared to dislocation loops. This is a further
confirmation that very little, if any, of the lattice parameter change observed during stage Q-2, runs 5 and 6, is due to the annealing of larger voids.

The third factor, sample thickness, has a large effect on the kind of dislocation loops found following stage Q-1 annealing. Das and Washburn\textsuperscript{31} studied the effects of sample thickness and found that for their water quenches there was an optimum sample thickness for obtaining faulted dislocation loops. Thin specimens can be easily bent on entering the quenching medium while thick specimens can undergo deformation because of large temperature gradients present during the quench. In both cases the deformation increases the proportion of perfect to faulted dislocation loops. In order to estimate the maximum diameter of aluminum wire which can be quenched without straining, a calculation similar to that by Van Bueren\textsuperscript{34} was performed. Results are shown in Table 1 together with the corresponding values of sample thickness for the different runs. The validity of this calculation is checked by comparing the results with Takamura's\textsuperscript{11} experimental study of quenching strains in gold rods. Reasonable agreement is found. The samples used for the present work are slabs 0.008- to 0.012-inch thick and 0.040-inch wide. According to the calculation, the samples in runs 4 and 5 were strained appreciably during the quench, and one should thus expect them to contain large numbers of perfect dislocation loops prior to anneal. On the other
<table>
<thead>
<tr>
<th>Run</th>
<th>Sample Thickness (inch)</th>
<th>Quenching Speed (°C/sec)</th>
<th>Calculated Critical Sample Diameter (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 3</td>
<td>0.008</td>
<td>&lt; 3000</td>
<td>&gt; 0.015</td>
</tr>
<tr>
<td>Run 4</td>
<td>0.012</td>
<td>4400</td>
<td>0.012</td>
</tr>
<tr>
<td>Run 5</td>
<td>0.012</td>
<td>5400</td>
<td>0.011</td>
</tr>
<tr>
<td>Run 6</td>
<td>0.009</td>
<td>3000</td>
<td>0.015</td>
</tr>
</tbody>
</table>

\(^a\text{Van Bueren}^{34}\)
hand, samples used in runs 3 and 6 were strained much less. Stage Q-2 in run 6 should thus correspond to the annealing of an appreciably larger number of faulted dislocation loops than the corresponding number in stage Q-2 of run 5. This is the same conclusion previously reached by considering the relative temperature at which perfect and faulted dislocation loops anneal.

Using the information gained on the defects present and the volume calculations outlined previously, a quantitative interpretation of the lattice parameter changes observed during runs 5 and 6 can now be made (Table 2). The vacancy concentration at thermal equilibrium at the quenching temperature is obtained from the work of Simmons and Balluffi. A quench rate curve obtained by Bass is very similar to the quenching curves obtained in this experiment (Fig. 14). Under these conditions, Bass found a 90% loss of free vacancies from their equilibrium concentration at 600°C. It can also be seen from the work of Bass that, for a high fractional vacancy loss, the number of vacancies lost is very insensitive to the factors affecting that loss. As a result, the estimate of the concentration of vacancies remaining after the quench, made from the results obtained by Bass can be considered reliable, and also applicable to the present analysis. For a cubic lattice containing a concentration $C_v$ of vacancies, the lattice parameter change $\Delta a/a$ is given by
Table 2. Interpretation of Lattice Parameter Changes During Runs 5 and 6

<table>
<thead>
<tr>
<th></th>
<th>Run 5</th>
<th>Run 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Thermal equilibrium $C_v$ at 600°C.$^a$</td>
<td>$4.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>2.</td>
<td>$\Delta a/a$ for the above concentration.$^b$</td>
<td>$-58 \times 10^{-6}$</td>
</tr>
<tr>
<td>3.</td>
<td>$C_v$ remaining after quench.$^c$</td>
<td>$0.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>4.</td>
<td>$\Delta a/a$ remaining due to $C_v$ in 3.$^b$</td>
<td>$-6 \times 10^{-6}$</td>
</tr>
<tr>
<td>5.</td>
<td>$\Delta a/a$ remaining after quench.$^d$ (Experimental)</td>
<td>$-55 \times 10^{-6}$</td>
</tr>
<tr>
<td>6.</td>
<td>$C_v$ forming dislocation loops during quench necessary to explain the discrepancy between 4 and 5.</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>7.</td>
<td>$\Delta a/a$ measured during stage Q-2.$^d$ as dislocation loops anneal. (Experimental)</td>
<td>$65 \times 10^{-6}$</td>
</tr>
<tr>
<td>8.</td>
<td>Total $C_v$ in dislocation loops.</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>9.</td>
<td>$C_v$ in dislocation loops after the quench + $C_v$ of vacancies in free state remaining after the quench. (Sum of 3 and 6.)</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$^a$Simmons and Balluffi
$^b$Using $V_f$ measured by Emrick and McArdle
$^c$Bass
$^d$This experiment
Figure 14. Temperature During Quench as a Function of Time
\[ \Delta a/a = C_v \Delta V_r / 3\Omega \]

where \( \Delta V_r = 0.36 \) for vacancies in aluminum. Since the final recovery of all quenched-in defects takes place during stage Q-2, the end of the recovery of \( \Delta a/a \) in stage Q-2 corresponds to the value of the lattice parameter in the undistorted state prior to the introduction of defects. Thus the value of \( \Delta a/a \), immediately after the quench, expected from the vacancy loss estimate, can be calculated. The same quantity, prior to stage Q-1 annealing, is available from the present data and any discrepancy between these values can be assigned to dislocation loops having formed during quenching. When one assumes a complete lattice relaxation around vacancies which form dislocation loops, given by

\[ \sum_{DL} \Delta V_r(DL) = - \Omega \sum_{DL} N, \]

one can calculate the number of vacancies in dislocation loops. The results are summarized in Table 2.

Table 2, line 1 minus line 6, shows that during the runs in the present work, the majority of the vacancies present at thermal equilibrium are lost to dislocation lines or voids during the quench. At the same time, a large number of dislocation loops are nucleated and these grow during the quench (line 6). On the other hand, in view of the agreement between lines 8 and 9 in Table 2, it can be
stated that all the vacancies left after the quench migrate to dislocation loops during stage Q-l.

As can be seen in Fig. 8 and 9, an unexpected initial drop in the lattice parameter in run 4 and a rise in run 5 occur. This change is not due to the deformations resulting from the handling of the specimen after quenching. No corresponding lattice parameter change is observed for run 3 (Fig. 7) in which the sample was purposely placed into a liquid nitrogen bath in a horizontal position to maximize thermal straining. This behavior appears to be the result of the recovery of samples which underwent quenching strain. Quenching stress is proportional to quenching rate and to the square of the sample thickness. It can be seen then from Table 1, that the samples in runs 4 and 5 underwent three times the stress of samples in runs 3 and 6. The complicated stress distribution over the samples could result in the x-ray beam falling on a part of the sample in one case where the recovery in the lattice parameter resulted in its increase, and on another part in another case where the recovery resulted in its decrease.

The effects of the same quenching strain can account for the differences in the stage Q-l annealing behavior observed in runs 4, 5, and 6. The presence and direction of local quenching stresses may have had an effect on the annealing temperature range of stage Q-l as well as on the size of Δa/a changes during that stage. In the case of run
5, a pre-stage Q-l recovery consisting of an increase in the lattice parameter may imply an accelerated clustering during quench. In the opposite case of run 4, Δa/a decreases prior to stage Q-l and a much larger stage Q-l follows probably indicating an opposite effect on the clustering during the quench. In fact, it can be seen that immediately after quenching 50% more vacancies are found in dislocation loops in run 5 than in run 6 (Table 2).

4.2 Line Shape Changes

It has been demonstrated by Borie that point defects, which produce small local distortions of the crystalline lattice, cause a reduction of the x-ray line intensities. However, a calculation of the intensity change due to the introduction of quenched-in vacancies shows the effect too small to be observed during the present study. The intensity changes observed are then likely to be the effect of larger vacancy clusters.

A decrease in intensity is observed in the initial portion of stage Q-l annealing for runs 4, 5, and 6. This can be explained by a theory of x-ray scattering by crystals containing dislocation loops as developed by Krivoglaz and Ryaboshka (hereafter referred to as KR). KR show that the expression for the scattering intensity of regular x-ray reflections contains an attenuation factor $e^{-2L}$. 
Under the present experimental conditions, for \( \frac{1}{4} a \langle 110 \rangle \) dislocation loops lying in the {111} planes, \( L \) is given by

\[
L_{DL} = 45N_{DL}R_0^3,
\]

where \( N_{DL} \) is the number of dislocation loops per cm\(^3\) and \( R_0 \) their average effective radius. The attenuation factor \( e^{-2L} \) thus has a strong dependence on the density of dislocation loops and even a stronger dependence on their radius. For individual vacancies, the order of magnitude of \( L \) is given by

\[
L_V \sim 45N_V(a/3^{\frac{k}{2}})^3
\]

where \( N_V \) is the number of vacancies per cm\(^3\), and \( a/3^{\frac{k}{2}} \) is the nearest neighbor distance in aluminum. For a typical vacancy concentration of \( 1.5 \times 10^{-4} \) (see Table 2), the above estimate for \( L_V \) is 0.005. Thus the factor \( e^{-2L} \) has no observable effect on the intensities. Since a dislocation loop of radius \( R_0 \) contains \( R_0^2/(a/3^{\frac{k}{2}})^2 \) vacancies one obtains

\[
L_{DL}/L_V \sim R_0/(a/3^{\frac{k}{2}}).
\]

This means that as vacancies cluster, the x-ray line intensity depends very much on the final size of clusters that grow, since \( L \) can change by many orders of magnitude for specimens with large dislocation loops.
KR show that when one introduces dislocation loops of such concentration and size that \( L << 1 \), the intensity of Bragg reflections decreases. This then explains the intensity behavior observed in the initial portion of stage Q-1 annealing for runs 4, 5, and 6. The inconsistency between the relative magnitudes of lattice parameter and intensity changes observed in the different runs can be explained by the fact that while lattice parameter changes are predominantly sensitive to the sum of the dislocation loop areas, intensity changes are more sensitive to dislocation loop sizes.

During the later portion of stage Q-1, run 6 shows a large increase in the integrated Bragg peak intensity (Fig. 10), even though no significant change in the lattice parameter or peak half-width occur at the same temperature. In Table 2 (run 6), \( 1.0 \times 10^{-4} \) is the concentration of vacancies in dislocation loops estimated to be present at the beginning of stage Q-1. For \( 10^{13} \) loops per cm\(^3\), a reasonable dislocation loop density, the average loop increases to 1200Å and the value of \( L_{DL} \) is 0.8. At the end of stage Q-1, the concentration of vacancies in loops increases to \( 1.5 \times 10^{-8} \). If the number of loops remains the same, \( R_0 \) now becomes 1500Å and \( L_{DL} = 1.5 \). These are very rough estimates since the dislocation loop density is not known and the values of \( L_{DL} \) depend strongly on the size of loops formed. However, one can see that during stage Q-1
annealing in run 6 it is likely that $L \sim 1$. The sample is then in a state of crystal distortion by dislocation loops in between the two extreme states examined by KR. These two states are defined by KR as that of slight crystal distortion ($L \ll 1$) and heavy crystal distortion ($L \gg 1$). A sharp increase in the observed integrated intensity is predicted by KR to occur in the transition region ($L \sim 1$). Such an increase is seen after annealing at $-15^\circ C$ (stage Q-1, run 6), and can be described in terms of an increase in $L$ due to a growth of the dislocation loop radii. The mechanism for this growth of dislocation loops at the end of stage Q-1 is uncertain from the present observations, since no simultaneous change in the lattice parameter is detected. One might speculate that very small clusters of vacancies, where considerable relaxation of the lattice has already occurred, are involved.

In the $L \gg 1$ case, an increase in both the width of the peak and in the intensity is described by KR and explained in terms of a rise in the diffuse scattering about the regular reflections as the distortion of the crystal increases. In the $L \ll 1$ case, KR describe a decrease in the integral intensity while the width of the x-ray reflections remains constant. After an anneal at $-65^\circ C$, however, the x-ray half-width in all three runs shows an increase as the peak intensity decreases. Thus, some apparent inconsistency exists between the description of KR and the present
results. A possible reason for the discrepancy may be that KR use the kinematic theory of x-ray reflection. This assumes an ideally imperfect crystal consisting of mosaic blocks 10,000Å on a side, separated by crystalline faults, such as groups of dislocation lines. Dislocation loop densities of $10^{13}$ to $10^{14}$ per cm³ result in an average spacing of 2000Å to 5000Å between dislocation loops. The mosaic structure in a real crystal can then be affected appreciably by the dislocation loops. Thus any change affecting the larger dislocation loops is likely to result in a change in the extinction property of the crystal. Such behavior was actually observed by Batterman, and the rocking curves obtained by him are similar to the rocking curves a and b in Fig. 11.

In the early portion of stage Q-2 annealing (Fig. 9 and Fig. 10), both intensity and half-width increase. At the same time, the lattice parameter begins a recovery which is characteristic of disappearing clusters. This can be explained in terms of larger vacancy clusters growing at the expense of some of the smaller ones. Such annealing behavior was actually observed by means of electron microscopy by Shimomura, and also discussed in detail by Edington and Smallman and Silcox and Whelan.

The sudden decrease in line width in the later stage of Q-2 annealing is consistent with the analysis by KR and with the results of electron microscopy in which all the
dislocation loops are observed to be shrinking and disappearing. According to the KR analysis, when going directly from a "highly distorted" crystal to a distortion-free crystal, the change in the integral intensity is expected to be absent. However, the effect of the dislocation loops on the extinction properties of the crystal explains the decrease in intensity actually observed. Further annealing at 210°C and 235°C has only a small effect on the lattice parameter, but causes large decreases in both line width and intensity. The disappearance of lattice defects in stage Q-2 can cause an unpinning of dislocation lines. Furthermore, as vacancies from the dissolving defects migrate to dislocation lines, these are observed under the electron microscope to untangle. As a result, dislocation lines are likely to climb. Thus the size of the mosaic structure of the crystal increases and the extinction property of the crystal is affected.

4.3 Summary

(1) Isochronal annealing of aluminum after quenching indicates that most of the changes in the lattice parameter, Bragg line intensity and half-width occur in the same two stages as previously observed by means of resistivity and electron microscopy.

(2) It appears that large thermal quenching strains show up as \( \Delta a/a \) recovery prior to stage Q-1 annealing.
(3) A large number of vacancies form dislocation loops which grow during the quench. This is supported by calculations based on the lattice relaxation around defects as well as interpretation of intensity and half-width data.

(4) The experimental results strongly suggest growth of dislocation loops during stage Q-1. Calculations based on $\Delta a/a$ data further indicate that all vacancies remaining after the quench migrate to dislocation loops.

(5) The behavior of Bragg line intensity and half-width measurements during early stage Q-2 annealing is attributed to the growth of large dislocation loops at the expense of small ones.

(6) The major part of stage Q-2 is attributed to the disappearance of dislocation loops. Bragg line intensity and half-width behavior supports this assignment. Lattice parameter changes indicate a recovery in the relaxation of the lattice around the dislocation loops. A consideration of the quenching atmosphere demonstrates that the formation of voids is suppressed in this experiment.

(7) Intensity and half-width measurements indicate that stage Q-2 is followed by a significant growth of the mosaic blocks in the crystal, probably due to a rearrangement and climb of dislocation lines.
LIST OF REFERENCES


